SECURITY CLASSIFICATION OF THIS PAGE

ORT DOCUMENTATION PAGE

1 AD-A222 405	1b. RESTRICTIVE MARKINGS: None
2	3. DISTRIBUTION/AVAILABILITY OF REPORT: Unlimited
2	
4. PERFORMING ORGANIZATION REPORT NUMBER(S): interim technical report #35	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION: Department of Chemistry	6b. OFFICE SYMBOL (If applicable)
7a. NAME OF MONITORING ORGANIZATION: Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code): Massachusetts Institute of Technology, 77 Mass. Avenue, Bldg. 6-335, Cambridge, MA 02139	7b. ADDRESS (City, State, and ZIP Code): Chemistry Division, 800 N. Quincy Street, Arlington, VA 22217
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: Office of Naval Research	8b. OFFICE SYMBOL (If applicable)
9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: N00014-84-K-0553	
8c. ADDRESS (City, State, and ZIP Code): Chemistry division, 800 N. Quincy Street, Arlington, VA 22217	10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
		051-579	

11. TITLE (Include Security Classification)

Face-Specific Interaction of MoS_4^{2-} with Oriented Crystals of (0001) CdX(X = Se, S)

12. PERSONAL AUTHOR(S)

James Hickman and Mark S. Wrighton

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
technical interim	FROM 5/89- TO 5/90	5/17/90	17

16. SUPPLEMENTARY NOTATION

Prepared for publication in Journal of the American Chemical Society

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	cadmium sulfide, cadmium crystals, spectrocopy pretreatment of etching procedures

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

See Attached Sheet

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unlimited
22a. NAME OF RESPONSIBLE INDIVIDUAL: Mark S. Wrighton	22b. TELEPHONE (Include Area Code): 617-253-1597 / 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete. — SECURITY CLASSIFICATION OF THIS PAGE

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Keywords: cadmium sulfides, cadmium crystals, spectroscopy, pretreatment of, etching procedure

Office of Naval Research

Contract NOOO14-84-K-0553

Task No. 051-597

Technical Report #35

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Prepared for Publication

in

Journal of the American Chemical Society

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[Prepared for publication as a Communication to the Editor of the Journal of the American Chemical Society]

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Abstract

Oriented (0001) CdX (X = S, Se) crystals selectively adsorb MoS_4^{2-} onto the Cd-rich faces. Binding of MoS_4^{2-} is effected by dipping the CdX crystals into CH_3CN containing 20 mM $[Et_4N]_2MoS_4$. Removal of the crystal from the solution followed by rinsing with CH_3CN leaves MoS_4^{2-} on the Cd- but not X-rich face of the crystal as detected by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The specificity for Cd-face vs. X-face binding is typically >5:1 as determined by XPS and AES data for both faces of the same crystal. S element maps for the MoS_4^{2-}-modified, Cd-face of CdSe crystals reveal non-uniform binding of MoS_4^{2-}. There is a correlation of the regions of MoS_4^{2-} binding with the crystal planes revealed in the pretreatment/etch procedure.

We wish to communicate that MoS_4^{2-} adsorbs selectively on the Cd-rich face of oriented crystals of (0001) CdX (X = S, Se) and that the binding to the Cd-rich face is non-uniform. We have used X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) to demonstrate the selectivity of the MoS_4^{2-} adsorption on CdX. In this work we have extended previous studies on the interaction of anionic S-donor species such as dithiocarbamates,[1] thiolates,[2-4] and polysulfides[5-7] on CdX crystals. Such studies reveal that anionic S-donors can strongly and favorably influence the CdX/electrolyte interface energetics to give highly efficient photoelectrochemical devices.[1-3,5-7]. Differential capacitance measurements have shown that the Cd-, but not S-, face of (0001) CdS interacts strongly with S^{2-}.[8] More recently it has been shown that $Fe(CN)_6^{3-/4-}$ interacts favorably only with the Cd-rich face of CdX.[9] This study was undertaken to better understand the role of crystal orientation in determining the degree of interaction of CdX with anionic S-donor compounds. We chose to investigate MoS_4^{2-} as an adsorbate, because of its high charge to size ratio.

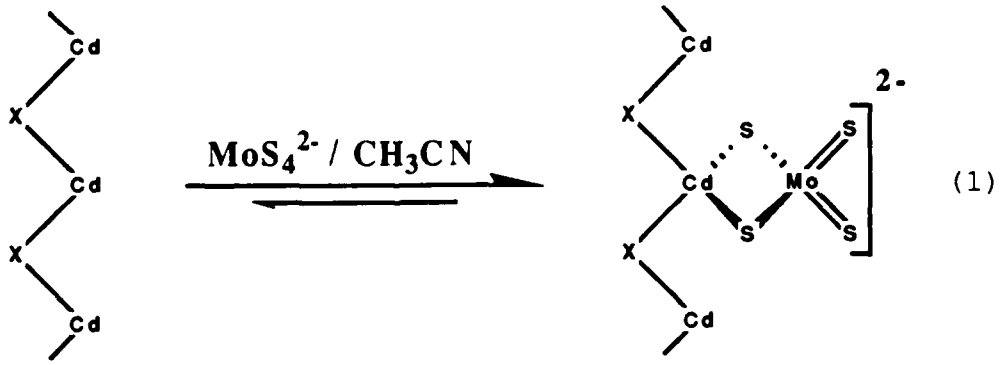
Experiments were carried out using n-type CdX single crystals (1-2 mm thick and 0.2-0.4 cm^2 in area from Cleveland Crystals, Cleveland, Ohio) cut perpendicular to the c-axis to expose the (0001) face. The CdX crystals were first cleaned in concentrated H_2SO_4 to remove C-containing

deposits. The CdS crystals were then etched in 12 M HCl[10] for 30 s and rinsed with copious amounts of H_2O and then with CH_3CN. The CdSe crystals were etched in a 3:1 mixture of $HCl:HNO_3$ for 15 s, rinsed with H_2O, and then exposed to a 1 M KCN solution for 5-10 min.[10] The crystals were finally rinsed with H_2O and then with CH_3CN. AES analysis of the etched CdX crystals indicates the presence of some adventitious C and O, but no other contaminating elements were detected.

The CdX crystals were modified with MoS_4^{2-} by immersing them for 5 min in a 20 mM solution of $[Et_4N]_2MoS_4$[11] dissolved in distilled and deoxygenated CH_3CN. The crystals were then rinsed with CH_3CN for 1-2 min and stored under vacuum prior to introduction into the spectrometer. The crystals were examined by XPS and/or AES.[12]

CdS crystals modified with MoS_4^{2-} were examined principally by XPS because the element Mo is much more easily detected by XPS than AES. CdSe crystals were examined by AES (for S) and XPS (for Mo and S). Both AES and XPS show selective binding of MoS_4^{2-} to the Cd-rich face of CdX. Representative XPS data are shown in Figure 1 for CdS. Spectra were taken on both sides of the same crystal to eliminate artifacts arising from differences between crystals, and essentially the same result was found for each of >10 independently prepared samples. The Mo signal on the Cd-rich face is at least five times that on the X-rich face. The peak energy of the Mo $3d_{5/2}$ signal is 232.6 eV (using

Cd^{2+} $4d_{5/2}$ at 405.1 eV as a reference) which is consistent with Mo(VI)[13] and suggests that the MoS_4^{2-} remains intact after adsorption onto the surface of the crystal. The Mo/S ratio and peak positions in the XPS of MoS_4^{2-}-treated CdSe are the same as for pure $[Et_4N]_2MoS_4$. The S 2s peak (on CdS) and Se 3s peak (on CdSe) in XPS measurements were used to calibrate the absolute magnitude of the Mo 3d peaks, and we conclude that there is roughly one monolayer of MoS_4^{2-} on the Cd-rich face of CdX. Prolonged washing of the MoS_4^{2-}-treated CdX with CH_3CN does lead to removal of the Mo signal. The results are consistent with reversible binding of intact MoS_4^{2-} to the Cd-rich face of (0001) CdX represented in equation (1).



(1)

The SEM of the Cd-rich face of CdSe, Figure 2, shows a surface with many sharp ridges, irregularities, and etch pits. The etch pits consist of planes of differing crystallographic orientation. Comparison of the S map from AES to the SEM indicates that the MoS_4^{2-} interacts only with certain features on the Cd-rich face of CdSe. This pattern of S AES signals does not arise from differential charging,

because the Cd map from AES is uniform over the region where there is significant variation of the S. The results for (0001) CdSe show that MoS_4^{2-} adsorbs selectively on the Cd-rich face, but the binding on the Cd-face is non-uniform.

Studies are in progress to pursue the relation between the extent of surface non-uniformity (and crystal orientation) and the magnitude of the flat-band potential shift of CdX in solvent/electrolyte media as a function of adsorbate (MoS_4^{2-}) concentration. Frequency dependent interfacial capacitance measurements[14] have been interpreted to mean that the Cd face of (0001) CdS is composed of regions with different flat-band potentials. Differences in surface morphology of the Cd-rich face and the S-rich face are revealed by SEM and may be a factor in the face selective binding of MoS_4^{2-}. For now, however, it is tempting to conclude that selective binding of MoS_4^{2-} occurs at sites that can best accommodate the structure represented in equation (1).

Aside from CdX/adsorbate interactions, several III-V semiconductor/adsorbate systems are of interest. These include GaAs functionalized with Ru,[15] Co,[16] and Os[17] and the selective modification of (111) InP on the P-rich face.[18] These systems are to be investigated by scanning AES to establish whether modification is uniform.

Acknowledgement. We thank the United States Department of Energy, Office of Basic Energy Sciences, Division of

Chemical Sciences for support of this research. We acknowledge use of XPS and Auger facilities acquired through the joint Harvard/M.I.T. University Research Initiative funded by the Defense Advanced Research Projects Agency.

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12. (a) Auger electron spectra were recorded on a PHI 660 Scanning Auger Microprobe employing a 15 KeV, 10-20 nA electron beam for excitation. SEM micrographs were recorded on the same instrument at 15 KeV and 1-2 nA electron beam excitation energy. Samples were attached and grounded to the stage with metal screws. (b) X-ray photoelectron spectroscopy was taken on an SSL 100 spectrometer. Samples were attached to the stage via metal clips. The Cd $3d_{5/2}$ peak (405.1 eV binding energy) was monitored as the reference and was used to correct for sample charging. The X-ray line used for excitation was the Al Kα line at 1486.6

eV. AES and XPS reference data for Cd, S, Se, and Mo can be found in: Handbook of Auger Electron Spectroscopy, 1978 (AES) and Handbook of X-ray Photoelectron Spectroscopy, 1979 (XPS) published by Perkin-Elmer Corp., Eden Prairie, MN.

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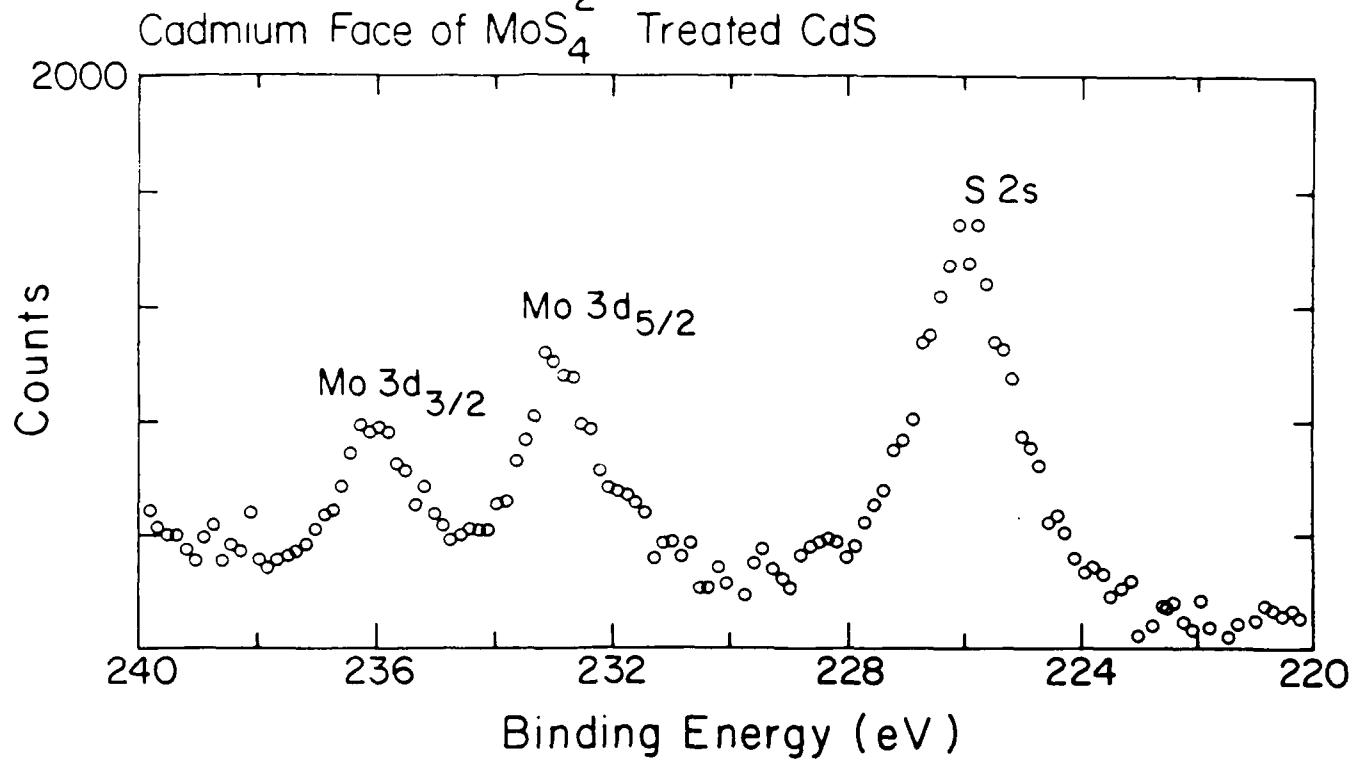
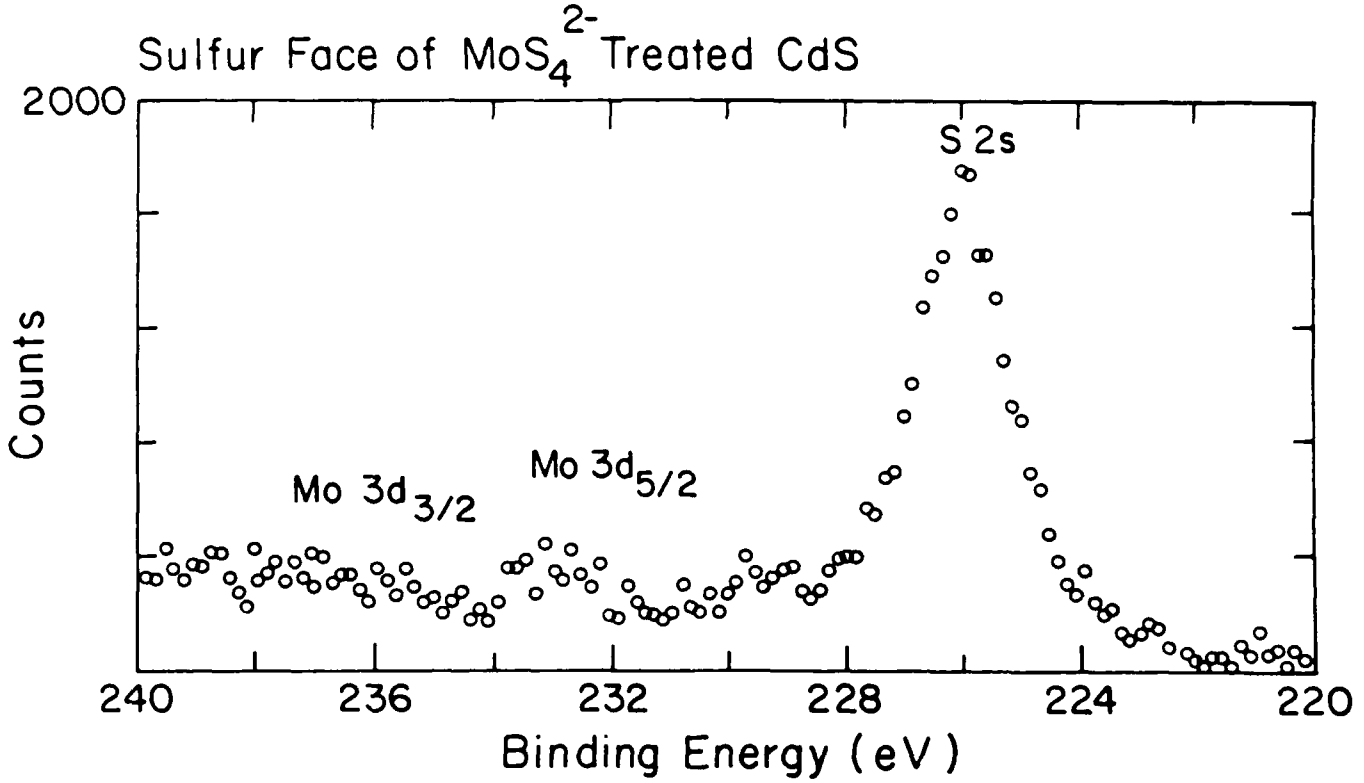
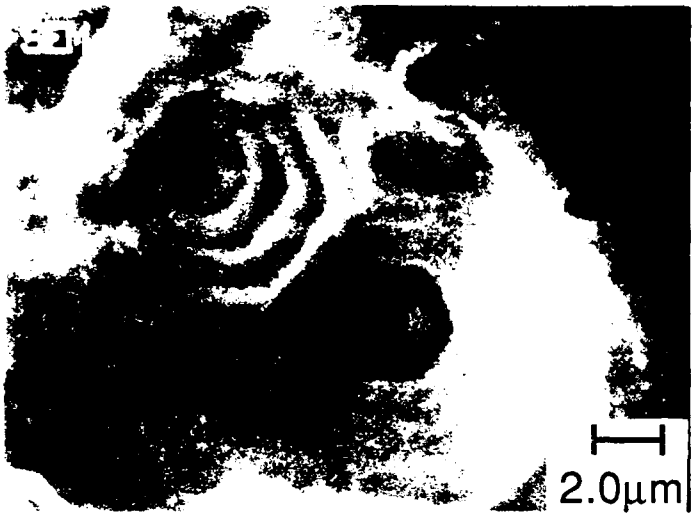
Figure Captions

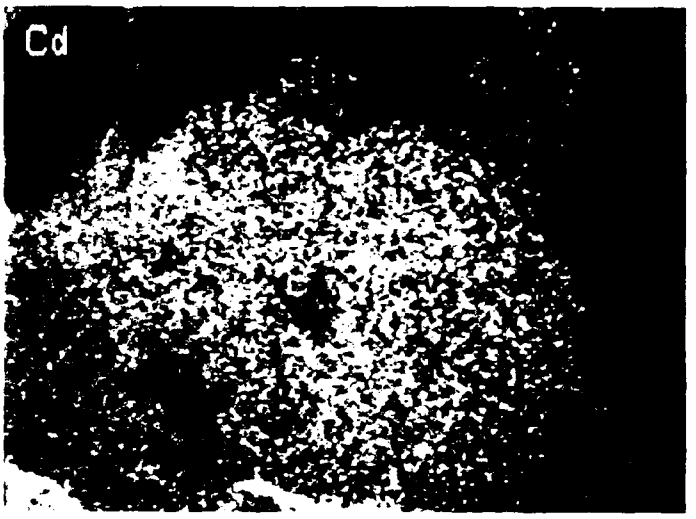
Figure 1. XPS data showing MoS_4^{2-} adsorption on only the Cd-rich face of oriented (0001) CdS.

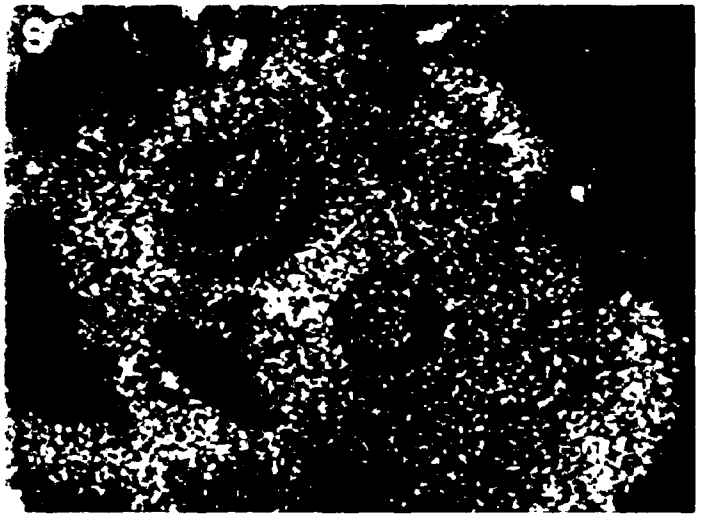
Figure 2. Three element maps (S, C, and Cd) of an etch-pit on the Cd-rich face of (0001) CdSe depicted in the SEM in upper left corner. The surface concentration of the elements is proportional to the brightness in each photograph. Carbon is adventitious from exposure to atmosphere after MoS_4^{2-} interaction. Note the Cd signal is obscured where the C coverage appears large.


Cadmium Face of MoS_4^{2-} Treated CdS
2000
Counts
S 2s
Mo $3d_{5/2}$
Mo $3d_{3/2}$
240
236
232
228
224
220
Binding Energy (eV)


Sulfur Face of MoS_4^{2-} Treated CdS
2000
Counts
S 2s
Mo $3d_{5/2}$
Mo $3d_{3/2}$
240
236
232
228
224
220
Binding Energy (eV)


2.0µm


Cd



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